

## Electronic Supplementary Information

### Anomalous Piezoelectric Response of Ferroelectric Mesocrystalline BaTiO<sub>3</sub>/Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> Nanocomposites Designed by Strain Engineering

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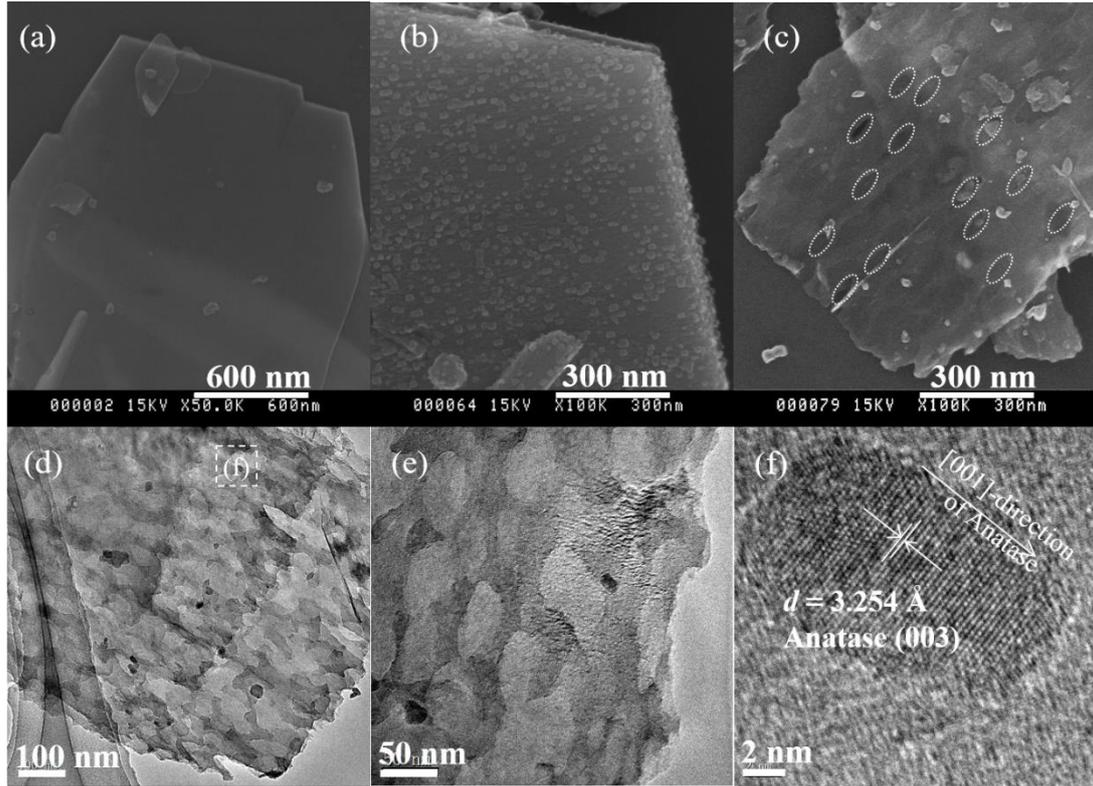
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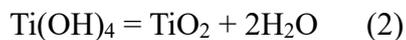
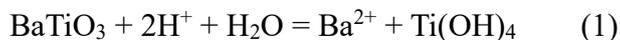


**Fig. S1.** (a, b, c) FE-SEM and (d, e, f) TEM images of (a) HTO precursor, (b) BT/HTO nanocomposite obtained by solvothermal treatment of HTO-Ba(OH)<sub>2</sub> mixtures with mole ratio of Ba/Ti = 0.5 at 150 °C for 12 h, (c, d, e, f) sample obtained by acid-treatment of BT/HTO nanocomposite with 2 M HCl solution for 12 h. (f) HRTEM image derived from white pane in TEM image (d).

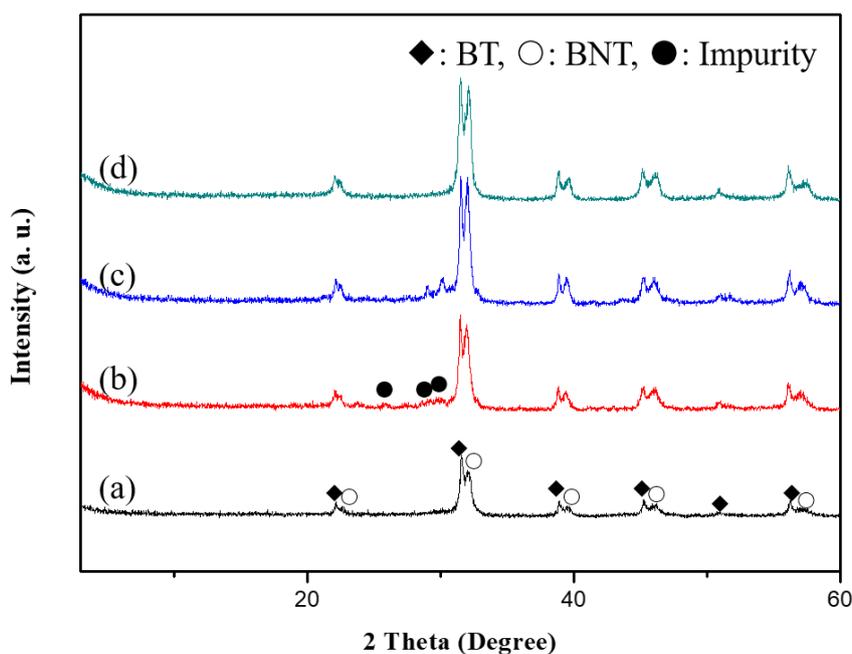
Fig. S1 shows the FE-SEM and TEM images of the HTO, BT/HTO as well as the acid-treated BT/HTO. It can be obviously seen that HTO crystal particle shows the platelike morphology with smooth surface, whereas many nanocrystals with a size of about 40 nm are observed on the surface of the platelike BT/HTO crystal particle. The nanocrystals on the surface correspond to BT phase.<sup>1-2</sup> After acid treatment of BT/HTO in a 2 M HCl solution, the BT nanocrystals were dissolved and removed away (Fig. 1). Seeing from Fig. 1S(c), the uniformly distributed pores in the platelike particle, marked by the white circles in the image, were formed.

The formation of the uniformly distributed pores with a size of about 50 nm can be confirmed also by TEM images (Fig. 1S (d and e)). According to the HRTEM result,

the nanoparticles with a size of about 10 nm on the porous HTO surface are anatase phase of TiO<sub>2</sub> nanocrystals. These TiO<sub>2</sub> nanoparticles are formed by dissolution reaction (1) of the BT nanoparticles and deposition reaction (2).



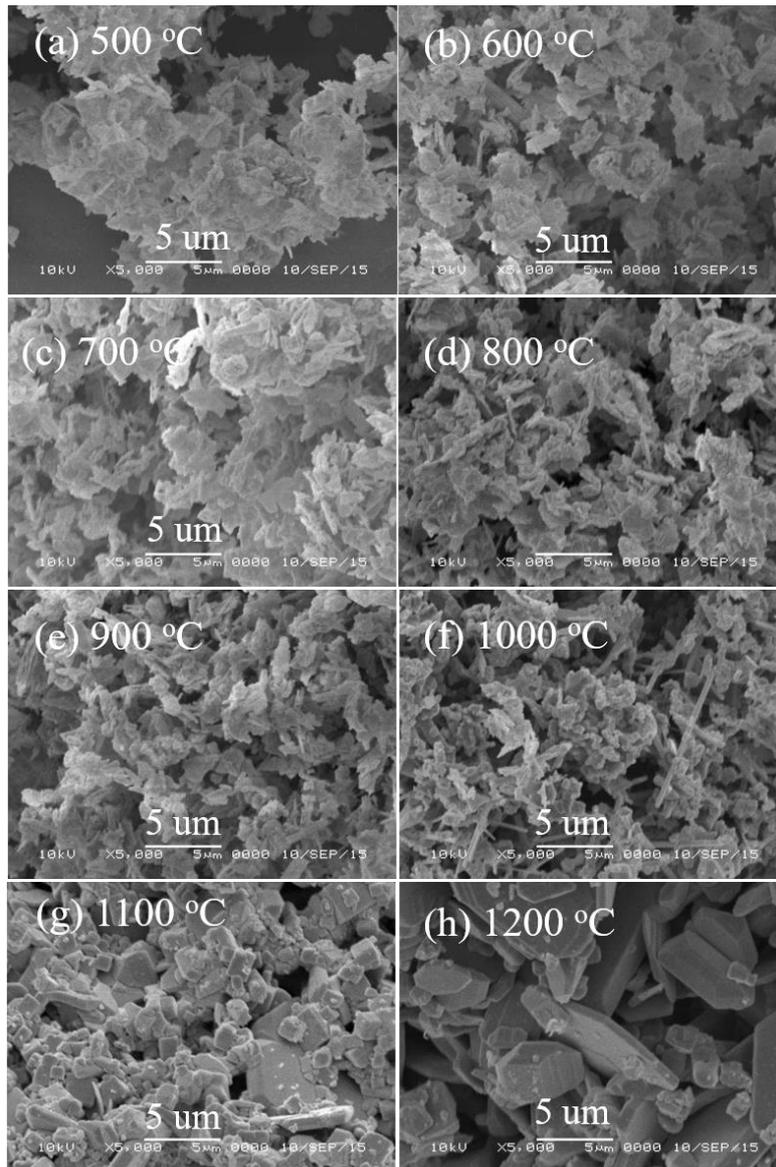
These results indicate that the BT in the BT/HTO nanocomposite formed by the topochemical process have a uniform distribution in the BT/HTO particle, which is a prerequisite for the formation of well-aligned mesocrystalline BT/BNT nanocomposite.



**Fig. S2.** XRD patterns of the samples obtained by heating treatments of (BT/HTO)-Bi<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> mixture with (a) stoichiometric mole ratio, (b) 10 % mole excess of Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, (c) 20 % mole excess of Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, and (d) 20 % mole excess of Bi<sub>2</sub>O<sub>3</sub> and 40 % mole excess of Na<sub>2</sub>CO<sub>3</sub> for formation of BT/BNT nanocomposite, respectively, at 700 °C for 3 h.

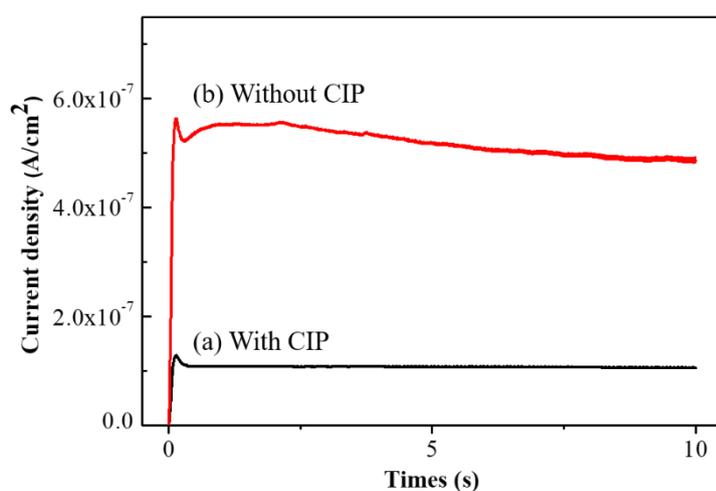
Under the conditions of stoichiometric mole ratio, 10 % and 20 % mole excess of Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in the (BT/HTO)-Bi<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> mixture, an impurity phase was

formed (Fig. 2S (a, b, c)) after the heating treatment, due to the evaporations of Bi and Na components in the mixture during the heat-treatment process. However, under the conditions of 20 % mole excess of  $\text{Bi}_2\text{O}_3$  and 40 % mole excess of  $\text{Na}_2\text{CO}_3$  in the mixture, only BT and BNT phases were formed. Therefore, 20 % mole excess of  $\text{Bi}_2\text{O}_3$  and 40 % mole excess of  $\text{Na}_2\text{CO}_3$  are the optimized condition for the preparation of BT/BNT nanocomposites, and this condition was used in the present study.



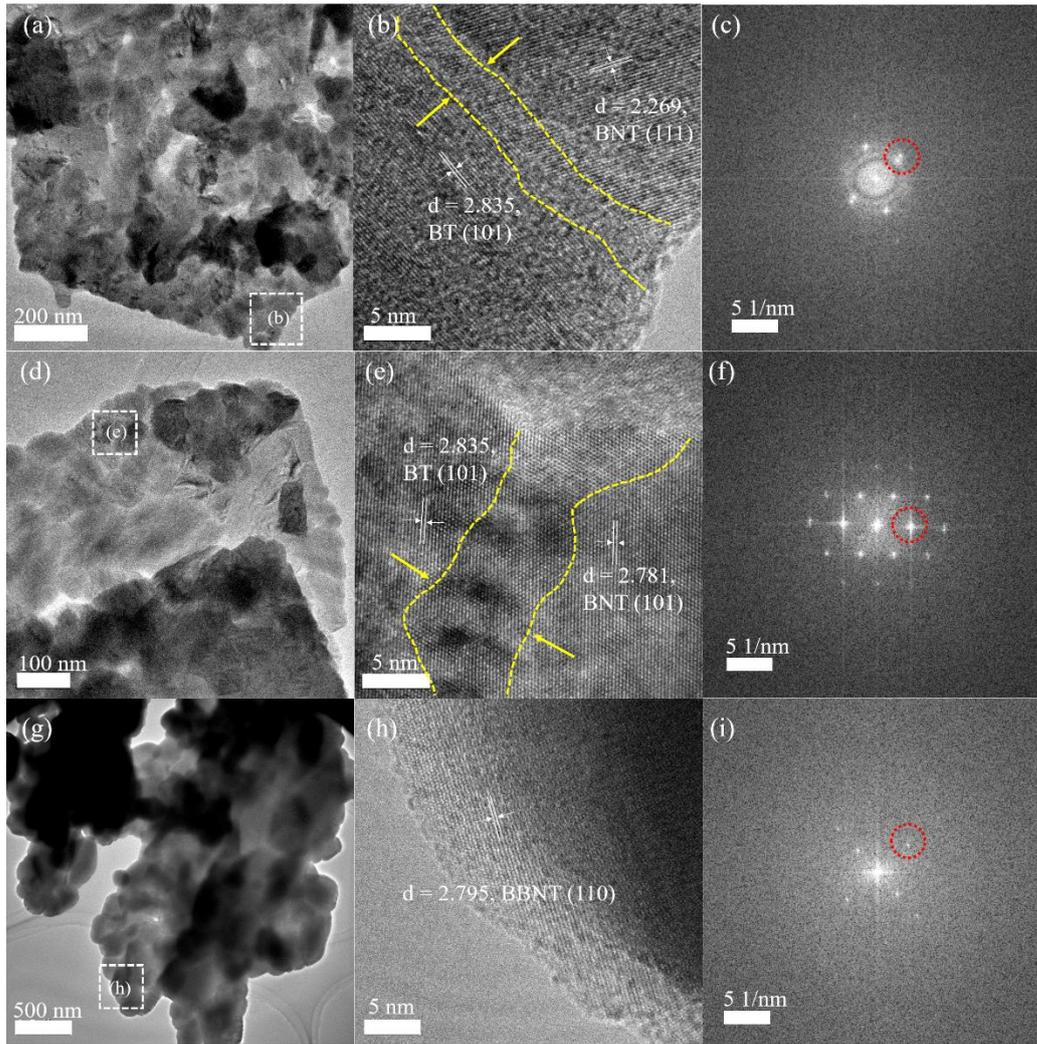
**Fig. S3.** SEM images of samples obtained by heat-treatments of the (BT-HTO)- $\text{Bi}_2\text{O}_3$ - $\text{Na}_2\text{CO}_3$  mixture at (a) 500, (b) 600, (c) 700, (d) 800, (e) 900, (f) 1000, (g) 1100, and (h) 1200 °C for 3 h, respectively.

Fig. S3 shows the samples obtained by heating treatments of the (BT-HTO)- $\text{Bi}_2\text{O}_3$ - $\text{Na}_2\text{CO}_3$  mixture at different temperatures for 3 h. The platelike morphology of the BT/HTO precursor can withstand up to 800 °C, begins to be destroyed above 800 °C, and changes to granular particles completely at 1100 °C.



**Fig. S4.** Plots of leakage current densities against time for the ferroelectric BT/BNT-700 pellet samples (a) with and (b) without CIP treatment at applied voltage of 6 kV/cm.

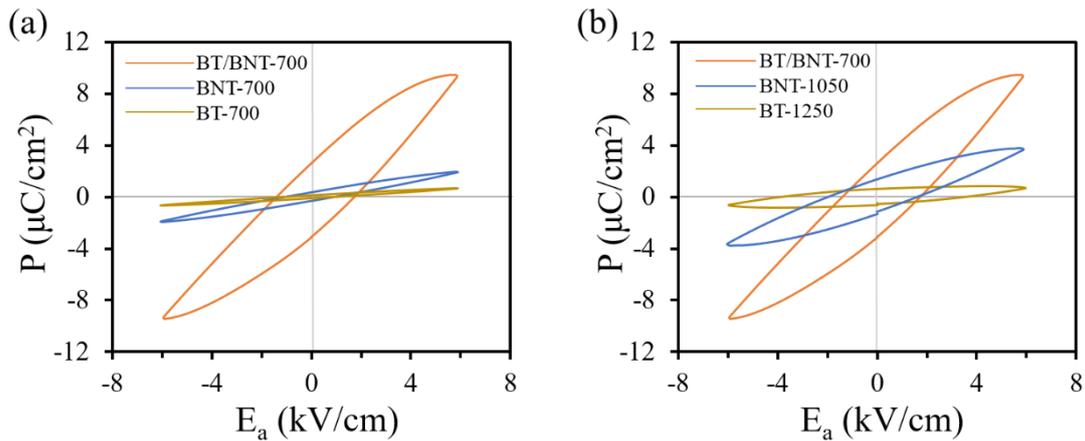
Fig. S4 shows the plots of the leakage current densities against time for the BT/BNT-700 pellet samples with and without cold isostatic pressing (CIP) treatment. It can be obviously seen that the current density of the BT/BNT-700 sample with the CIP treatment reduces to about 1/5 of that of the sample without the CIP treatment.



**Fig. S5.** (a, d, g) TEM images and (b, e, h) HRTEM images of BT/BNT-700, BT/BNT-800, and BT/BNT-1000, respectively. (b, e, h) HRTEM images are an enlarged image derived from white pane in (a, d, g) TEM images, respectively, and (c, f, i) FFT pattern obtained from the whole region of HRTEM (b, e, h), respectively.

A TEM observation was employed to attest the phase transition process from BT/BNT nanocomposite to BBNT solid solution at the interface between the BT and BNT phases in detail, as shown in Fig. S5. As for the BT/BNT-700 sample, the BT/BNT interface can be observed in a narrow area, inside the yellow lines in Fig. S5(b). Clear two sets of diffraction points generated in the FFT pattern (Fig. S5(c)) correspond to BT and BNT phases, respectively, which agrees well with the XRD

result (Fig. 3) and the SAED result (Fig. 4(f)). For the BT/BNT-800 sample, the HRTEM image shows a wider and more ambiguous interface area, inside the yellow lines in Fig. S5(e), which means formation of BBNT solid solution phase around the interface by diffusions of  $\text{Ba}^{2+}$  of BT and  $\text{Na}^+$  and  $\text{Bi}^{3+}$  of BNT, respectively. The two sets of diffraction points are getting closer and represent a large flare in the FFT pattern of the BT/BNT-800 sample (Fig. S5(f)), which further confirmed that the contiguous phase transformation at the heteroepitaxial interface between BT and BNT phases. According to the XRD result (Fig. 3), the BT/BNT nanocomposite transformed into the BBNT solid solution when the heating temperature was elevated to 1000 °C. Only one phase and one set of diffraction points were observed in HRTEM and FFT pattern (Fig. S5(h, i)), respectively, for the BT/BNT-1000 sample.

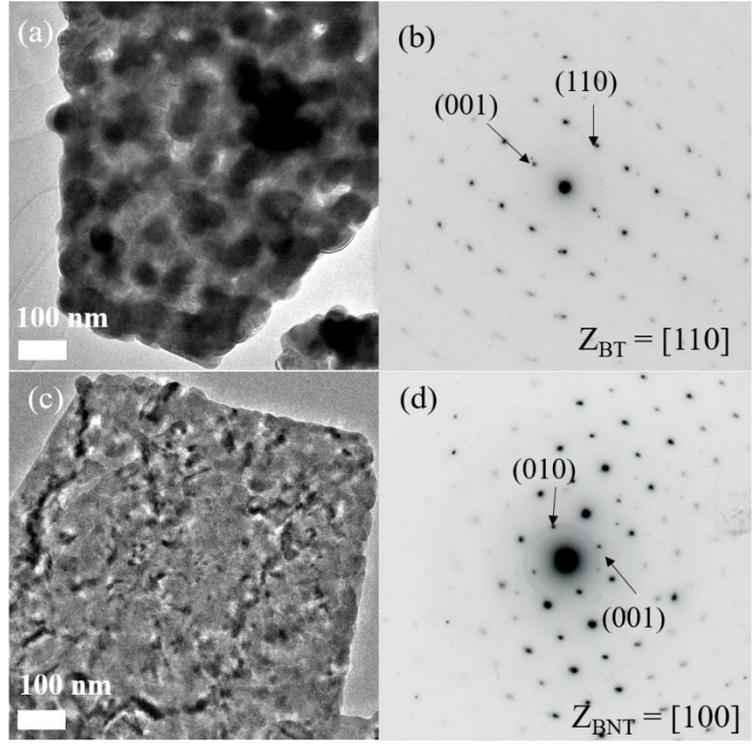


**Fig. S6.** P-E hysteresis loops of the pellet samples of (a) BT-700, BNT-700 and BT/BNT-700 as well as (b) BT/BNT-700, BNT-1050 and BT-1250 measured at 100 Hz.

Fig. S6 shows the P-E hysteresis loops of the pellet samples of BT-700, BNT-700

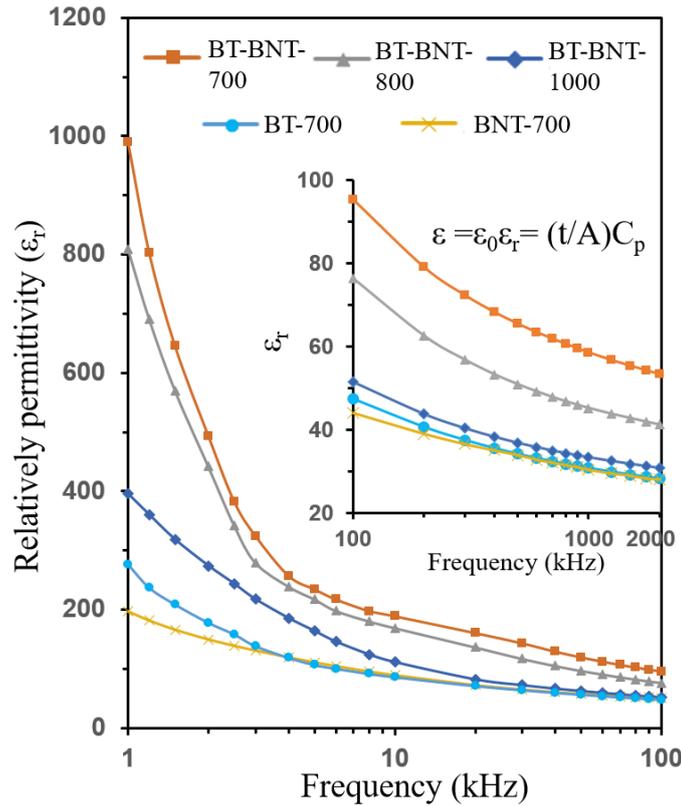
and BT/BNT-700 as well as BT/BNT-700, BNT-1050 and BT-1250 measured at 100 Hz. As we can see (Fig. S6 (a)), all the samples show the ferroelectric-like behavior, whereas the BT-700 and BNT-700 samples show a much smaller remnant polarization value than that of BT/BNT-700 nanocomposite. To further confirm the effect of the heteroepitaxial interface of BT/BNT nanocomposite on ferroelectric response, the BT-1250 and BNT-1050 samples were also prepared and measured (Fig. S6 (b)). The BT/BNT-700 sample still shows a amazing ferroelectric response, which has almost a double and triple remnant polarizations compared to the BT-1250 and BNT-1050, respectively. These results indicate that the introduction of the heteroepitaxial interface into the BT/BNT nanocomposite strengthens the ferroelectric response of the mesocrystalline BT/BNT nanocomposite.

The unsaturated P-E curves are due to the low electric field excitation. The high-density pellet sample of the BT/BNT nanocomposite is difficult to be prepared because the sintering temperature is low. The high electric field cannot be applied on such low-density sample due to large leakage current.



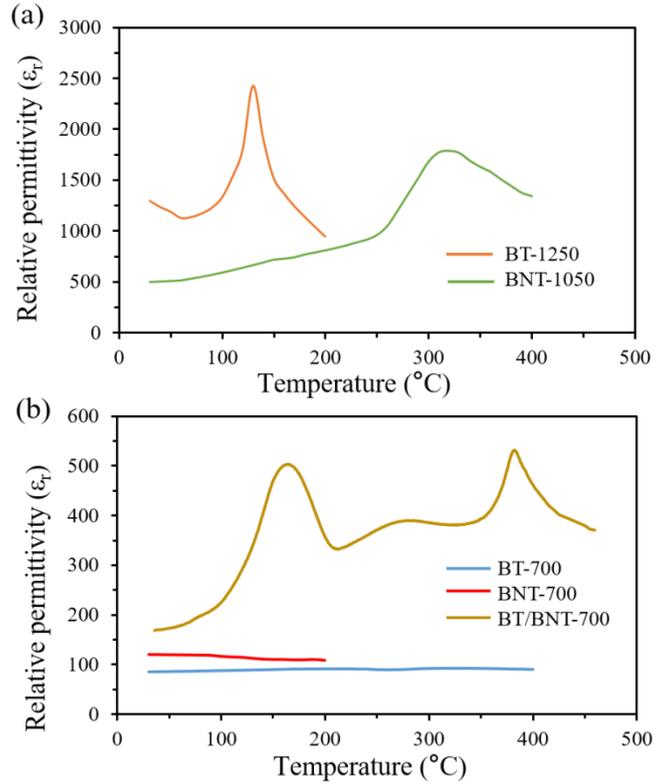
**Fig. S7.** (a, c) TEM images and (b, d) SAED spots patterns of (a, b) BT single phase mesocrystal sample BT-700 and (c, d) BNT single phase mesocrystal sample BNT-700.

For the ferroelectric behavior comparison with BT/BNT nanocomposite, BT and BNT single phase mesocrystals were prepared. Fig. S7 shows the TEM images and SAED spot patterns for the BT-700 and BNT-700 samples. It can be obviously seen that both of the samples show the well-shaped platelike morphology, and platelike particles are constructed from the BT and BNT nanocrystals with a size of about 60 and 50 nm, respectively. The platelike particles show the single crystal like SAED spot patterns with the orientation direction along the [110] and [100], respectively.



**Fig. S8.** Variations of relative permittivities for the pellet samples prepared by heat-treatment of (BT/HTO)-Bi<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> mixture at different temperatures for 3 h, and BT and BNT pellet samples prepared by heat-treatments at 700 °C for 3 h, respectively.

BT-700 and BNT-700 show relative small  $\epsilon_r$  values and small frequency dependences in the low frequency range because their very weak ferroelectricity. BT/BNT-700 sample exhibit a larger  $\epsilon_r$  value and larger frequency dependence in the low frequency range due to its strong ferroelectricity originating from the heteroepitaxial BT/BNT interface. The decrease of the permittivity of the samples prepared above 800 °C is ascribed to the partly transformation of BT/BNT nanocomposite into the BBNT solid solution. These results indicate that the mesocrystalline BT/BNT nanocomposite exhibits an advantage on the improvement of the dielectric response.



**Fig. S9.** Temperature dependences of the relative permittivity ( $\epsilon_r$ ) of (a) BT-1300 and BNT-1050, and (b) BT-700, BNT-700, and BT/BNT-700 pellet samples at 10 kHz.

The BT-1250 and BNT-1050 samples exhibit a maximum  $\epsilon_r$  value at around 130 and 320 °C, respectively, which correspond to their Curie temperatures ( $T_c$ ) or phase transitions from ferroelectric phase to paraelectric phase. However, BT-700 and BNT-700 samples show a character of the paraelectric, where without maximum  $\epsilon_r$  value in the temperature range measured, due to small crystal sizes of about 60 or 50 nm, which are the pseudo-cubic lattice of non- or weak ferroelectric. Surprisingly, BT/BNT-700 pellet sample shows three phase transition peaks at 160, 270, and 380 °C, respectively. The  $\epsilon_r$  peaks at around 160 and 380 °C can be assigned to the  $T_c$  of BT and BNT phases in the nanocomposite, respectively, although the crystal size of BT and BNT nanocrystals in BT/BNT-700 are almost the same as those in BT-700 and BNT-700. The result suggests that BT and BNT nanocrystals in the BT/BNT

nanocomposite change from paraelectric to ferroelectric by introducing the lattice strain at the BT/BNT interface. The new phase transition at around 270 °C can be assigned to BT/BNT interface or a distorted BBNT phase between BT and BNT phases as shown in Figs. 7(b) and S5(e). This phase transition was observed for the first time in the mesocrystalline nanocomposite.

## References

1. Q. Feng, M. Hirasawa and K. Yanagisawa, *Chem. Mater.*, 2001, **13**, 290-296.
2. D. Hu, H. Ma, Y. Tanaka, L. Zhao and Q. Feng, *Chem. Mater.*, 2015, **27**, 4983-4994.